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EFFECT OF THE INTERCRYSTALLINE INTERFACE ON THE STRENGTH OF CORUNDUM CERAMICS

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An equation is proposed for the calculation of the strength of intercrystalline corundum materials depending on the intercrystalline interface energy and the size of the crystals. It is demonstrated that as the crystal interface keeps increasing, the strength of the material will be determined by the crystallography of particles. It is experimentally established that by increasing the Cr₂O₃ content in an additive introduced in the Al₂O₃–Cr₂O₃–ZrO₂ system, it is possible to increase the strength of corundum materials by developing conditions for denser coalescence of crystals.

The propagation of cracks in sintered materials is determined by the size, shape, and coherence of the structural components and to a large extent depends on the rate of sample loading. Under slow loading determining the weakest structural link, the fracture in most ceramic materials will be intercrystalline.

Considering the Griffiths equation for the case of destruction of monocrystals, the value $2\gamma_1$ is the work of adhesion, i.e., the work done on creating two new surfaces:

$$\sigma_m = \sqrt{\frac{2\gamma_1 E}{\pi c}}, \quad (1)$$

where σ_m is the strength of the single crystal, γ_1 is the surface energy of the solid body, E is the modulus of elasticity, and c is the crack length.

In the case of propagation of the crack along the crystal boundaries, the adhesion work will be equal to $2\gamma_1 - \gamma_{11}$ (γ_{11} is the energy of the intercrystalline interface); then the strength of the intercrystalline interface will be

$$\sigma_{int} = \sqrt{\frac{(2\gamma_1 - \gamma_{11})E}{\pi c}}. \quad (2)$$

Dividing Eq. (2) by Eq. (1), we obtain

$$\sigma_{int} = \sigma_m \sqrt{\frac{2\gamma_1 - \gamma_{11}}{2\gamma_1}}, \quad (3)$$

hence it follows that as the intercrystalline energy decreases, the strength of the intercrystalline interface will grow. A de-

crease in the intercrystalline energy takes place as a result of the modification of the structure of boundary layers in smoothing the asymmetry of the force field of the contacting particles, and in doing so, intercrystalline structures with high density of strong oriented bonds are formed.

Since the intercrystalline interface designated as γ_{11} has a certain structure, volume, and strength, based on the mixture rule one can write

$$\sigma V = \sigma_m V_m + \sigma_{int} V_{int}, \quad (4)$$

where σ is the strength of the polycrystalline body, and V , V_m , and V_{int} are the volume of the polycrystalline body, the monocrystal, and the intercrystalline interface, respectively.

By expressing σ_m from Eq. (4) through substituting the obtained expression into expression (3), as well as expressing the respective volumes through the size of the crystals, we obtain

$$\sigma_{int} = \frac{\sigma}{\left(\frac{d-\delta}{d}\right)^3 \left[\left(\frac{2\gamma_1}{2\gamma_1 - \gamma_{11}} \right)^{1/2} - 1 \right] + 1}, \quad (5)$$

where d is the crystal diameter, and δ is the surface-layer thickness.

It follows from Eq. (5) that the value σ characterizes the maximum strength of the particular material, to which the strength of the intercrystal interface is approaching, depending on the decrease in the interface volume and energy. Therefore, one can assume that the σ -strength characterizing the material with intercrystal energy $\gamma_{11} \rightarrow 0$. In other words, a polycrystalline material with the maximal coalescence of the crystals to each other has the maximum strength. The

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maximum blending strength for corundum materials $\sigma \approx 750$ MPa [1]. Since the strength of the interface, which is the weakest link, determines the strength of the material, i.e., $\sigma_{\text{mat}} = \sigma_{\text{int}}$, one can calculate the strength of various materials, knowing certain initial data.

Thus, the strength of a corundum material with a crystal size of 3 μm and thickness of the surface layer ≈ 0.005 μm (the Bailby layer) [2] will be equal to 540 MPa in calculating the intercrystalline energy from the ratio

$$\gamma_{11} = 2 \cos \frac{\varphi}{2},$$

where φ is the equilibrium dihedral angle, for corundum material $\approx 120^\circ$ [3].

It should be noted that the strength of the material can be below the estimated value due to an increment in the interface energy by a certain additional energy value, depending on the disorientation of the crystals and their syngony, which is the most clearly manifested with an increasing crystal size. Such an increment can be equal up to an energy value of $\approx \gamma_1$ [4, 5].

The distribution of dihedral angle sections for fine-crystalline particles (round particles with low anisotropy) has a certain sharply expressed mode characterizing a certain value of the dihedral angle, which is mostly determined by the values γ_{11} and γ_1 . The particle shape in corundum materials changes from round to prismatic as the particle size increases. Such particles are characterized by sharply expressed crystallographic anisotropy, which decreases the coherence of crystals, whereas dihedral angles are mainly determined by the crystallography of the particles [5].

A decrease in the coherence of crystals in large-crystalline materials and an increase in the stresses at the crystal interface caused by the heat-expansion anisotropy produce a sharp decrease in strength. The evaluation of the strength of large-crystalline materials in accordance with Eq. (5) is rather approximated, since it is difficult to assess the change in the effect of particle crystallography on the interface energy value and, accordingly, on the decrease in the coherence of particles in transition from a fine-crystalline to a large-crystalline material. Thus, assuming that in a large-crystalline corundum material with the crystal size around 20 μm and prismatic shape of the crystals, the value γ_{11} is approximately $0.5\gamma_1$ higher than in the fine-crystalline material, the estimated strength will be ≈ 350 MPa.

In the general case, the strength of the interface contact depends on the value $(2\gamma_1 - \gamma_{11})$ [4]. Correlating it with $2\gamma_1$, i.e.

$$\frac{2\gamma_1 - \gamma_{11}}{2\gamma_1}, \quad (6)$$

this particular value will characterize the interface contact strength with respect to the strength of the material without interface, or the relative density of formation of direct bonds,

which is the higher, the greater the ratio (6) is, i.e., the lower the value γ_{11} .

It is possible to lower the value γ_{11} using different methods, for instance, by the hot compression method, including hot isostatic compression, as well as by introducing various additives regulating the coalescence of crystals [3, 6]. The study in [6] considered the effect of additives in the $\text{Al}_2\text{O}_3 - \text{ZrO}_2$ system on the strength of corundum ceramics, depending on the content of microadditives regulating the value γ_2 (the surface tension of the liquid phase) of the additive and the value γ_{12} (the surface energy in the contact site between the solid and liquid phases). The formation of strong direct crystal – crystal bonds is possible in liquid-state sintering, when the following inequality is satisfied [5]:

$$\gamma_{11} \leq 2\gamma_{12} \cos \frac{\varphi}{2}. \quad (7)$$

By varying the values γ_{12} , γ_2 , and, consequently, γ_{11} by varying the ratio of the additive components, one can significantly increase the strength of the material. Thus, as the weight content of Cr_2O_3 varied from 0 to 15% with respect to other components of the system $\text{Al}_2\text{O}_3 - \text{ZrO}_2$ (1 wt.%), the strength of corundum ceramics grew from 380 to 470 MPa, respectively. It is known [7] that a solid solution is formed in the $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3 - \text{ZrO}_2$ system between the components Al_2O_3 and Cr_2O_3 , whereas these components are virtually insoluble in ZrO_2 . Based on the above, it can be assumed that as the Cr_2O_3 content in the system $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3 - \text{ZrO}_2$ increases, the surface tension of the melted additive in accordance with the additivity rule will grow, since the surface tension in the system $\text{Al}_2\text{O}_3 - \text{Cr}_2\text{O}_3$ grows as well with an increasing Cr_2O_3 content [8]. An increase in γ_2 of the additive leads to increasing compressive capillary pressure between the particles [9] in accordance with the equation

$$F = \pi d \sigma_2 \cos \varphi. \quad (8)$$

When inequality (7) is satisfied in the case of good wetting of the additive, there are prerequisites for the formation of sites with dense coalescence between the crystals ($\gamma_{11} \rightarrow \min$). Furthermore, a certain amount of Cr_2O_3 from the additive is dissolved in corundum crystals, forming a solid solution on their surface, which increases γ_1 [9]. A decrease in γ_{11} and an increase in γ_1 will enhance the strength, due to the increased density of direct bonds between the crystals [expression (6)]. In this case, one can estimate the strength increment in accordance with Eq. (5) for the known values of γ_{11} and γ_1 , which can be determined by analysis of the ceramic structure (γ_{11}) and by direct physical measurements (γ_1).

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